THREE NOTES ON THE QUANTUM THEORY OF APERIODIC EFFECTS

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Abstract

In Section 1 it is shown that the normalization of the characteristic functions corresponding to a continuous spectrum, which has been introduced by Hellinger and Weyl, satisfies the requirements of the δ-normalization of the Dirac-Jordan transformation theory. It is further shown that this normalization makes the flux to and from infinity of systems for which an integral of motion β lies in the little range $\Delta\beta'$ equal to

$$(\partial E/h\partial\beta')\Delta\beta'.$$

In Section 2 the condition for the validity of classical mechanics in the form grad $\lambda << 1$, where λ is the instantaneous wave length $\lambda = (h/2\pi)[2M(E-U)]^{-1/2}$, is applied to establish Rutherford's formula for the scattering of α-particles.

In Section 3 a method is developed for computing the transition probabilities between states of the same energy, and which are represented by almost orthogonal eigenfunctions. The theory is applied to the ionization of hydrogen atoms in a constant electric field. The period of ionization in a field of 1 volt per cm is $10^{10^{10}}$ sec. The bearing of such transitions on the problem of metallic conduction is discussed.

THE normalization of continuous spectra has been formulated mathematically by Hellinger and Weyl; and it has been shown that this may be applied to a large class of quantum-mechanical problems without inconsistency.[1] The problem can, however, be treated a good deal more simply and generally. It may be formulated as follows: The δ-normalization required by the Dirac-Jordan transformation theory[2]

$$\int_B \{\alpha'/\beta'\}\, d\beta' \{\beta'/\alpha''\} = \delta(\alpha'-\alpha'') \tag{1a}$$

$$\int_A \{\beta'/\alpha'\}\, d\alpha' \{\alpha'/\beta''\} = \delta(\beta'-\beta'') \tag{1b}$$

means

$$\int_{\Delta\alpha''} d\alpha'' \int_B \{\alpha'/\beta'\}\, d\beta' \{\beta'/\alpha''\} = \begin{cases} 1 \text{ if } \alpha' \text{ lies in } \Delta\alpha'' \\ 0 \text{ otherwise} \end{cases} \tag{2a}$$

$$\int_{\Delta\beta''} d\beta'' \int_A \{\beta'/\alpha'\}\, d\alpha' \{\alpha'/\beta''\} = \begin{cases} 1 \text{ if } \beta' \text{ lies in } \Delta\beta'' \\ 0 \text{ otherwise} \end{cases} \tag{2b}$$

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[1] See J. R. Oppenheimer, Zeits. f. Physik **41**, 268 (1927); the method of this paper is an extension of that outlined in the footnote on page 270. The necessary references are given in this paper.

[2] A is the range of characteristic values of α, etc. $\{\alpha'/\beta'\}$ is the transformation function from α to β, with arguments α' and β'. Cf. P. A. M. Dirac. Proc. Roy Soc. **A113**, 621 (1927) who uses (α'/β').

Now the integrals in (1) and the inner integrals in (2) do not converge, so that the normalization in its present form is meaningless. We obtain Weyl's normalization if we interchange the order of integration in (2a), (2b); and the transformation functions so normalized have all the required properties. In particular the probabilities computed from them are invariant under a point-transformation of the form $\beta_1' = f(\beta')$; $\alpha_1' = g(\alpha')$, i e , changes of scale.[3]

The physical interpretation of (1) is analogous to that of the normalization of point spectra: the probability that the system has simultaneously the values β', β'' is zero if $\beta' \neq \beta''$; the total probability that it has a β near β' is unity. But in aperiodic phenomena, like the photoelectric effect, or a collision problem, what one observes is not the total number of particles somewhere in the infinite configuration space which satisfy a given condition, but their flux to or from infinity: the number of particles entering or leaving the system from "infinity" per unit time. That, when α or β, say β, is a constant of integration,[4] such an interpretation of (1) must be possible, is suggested by the following argument: Consider a system initially in a discrete state, and subject to a perturbation which dissociates it. If one uses the characteristic functions normalized by (2) one can find the probability of a system leaving the discrete state per unit time for a given range $\Delta\beta'$; this must also be equal to the number going to infinity per unit time in the same range, so that the normalization (2) may be regarded as determining the flux to infinity for the state β'. For a special kind of characteristic function this was verified in the previous paper, but it can, of course, be established quite generally. In this paper we shall show (a) that Weyl's form of (2) enables one to obtain the continuous matrices one needs, e.g., for the perturbation theory; and (b) that it makes the flux to and the flux from infinity in a range $\Delta\beta'$ equal to $(1/h)(\partial E/\partial\beta')\Delta\beta'$, in accordance with the requirements of quantum statistics. The method provides an analytical rule for the normalization which is considerably simpler than Weyl's.

The Weyl-Hellinger form for (2b) is

$$N = \int_A \Delta_1\Theta(\beta')d\alpha'\Delta_2\Theta^\dagger(\beta'') = {}_1\Delta_2\beta' \tag{2b'}$$

where

$$\Delta_1\Theta^\dagger(\beta') = \int_{\Delta_1\beta'} d\beta'\{\alpha'/\beta'\}$$

$$\Delta_2\Theta(\beta'') = \int_{\Delta_2\beta''} d\beta''\{\beta''/\alpha'\}$$

and where ${}_1\Delta_2\beta'$ is the common part of $\Delta_1\beta'$ and $\Delta_2\beta''$. From this follows (a) that $N=0$ if $\Delta_1\beta'$ and $\Delta_1\beta''$ do not overlap, and (b) that

[3] The proof that the normalized transformation functions have this property is given by P. Jordan, Zeits. f. Physik **41**, 797 (1927).

[4] The normalization (2), (3) is, of course, applicable even when this is not the case.

$$N/\Delta\beta' = 1 \tag{2b''}$$

for $\Delta_1\beta' = \Delta_2\beta'' = \Delta\beta'$.

This last form (2b''):

$$\int_A \{\alpha'/\beta'\}\, d\alpha' \Delta\Theta^\dagger(\beta') = 1 \quad \text{(when } \beta' \text{ lies in } \Delta\beta') \tag{3}$$

is just the condition that the matrix components of a function $F(\alpha')$, which are defined by

$$F(\alpha')\{\alpha'/\beta'\} = \int_B F(\beta'\beta'')\, d\Theta^\dagger(\beta'') \tag{3a}$$

may be given by

$$F(\beta'\beta'') = \int_A \{\alpha'/\beta'\}\, d\alpha' F(\alpha')\{\beta''/\alpha'\}\,. \tag{3b}$$

For (3a) yields

$$\begin{aligned} \int_A \{\beta'''/\alpha'\}\, d\alpha' F(\alpha')\{\alpha'/\beta'\} &= \int_A \{\beta'''/\alpha'\}\, d\alpha' \int_B F(\beta'\beta'')\, d\Theta^\dagger(\beta'') \\ &= F(\beta'\beta''') \qquad \text{by (3)}\,. \end{aligned} \tag{3c}$$

On the other hand we may derive this result, and thus (3), by a limiting process. If we take the domain A of α bounded ($-a \leqq \alpha' \leqq +a$), and make $\{a/\beta'\} = \{-a/\beta'\}$, the characteristic values of β become discrete:

$$F(\alpha')\{\alpha'/\beta'\} = \sum_{\beta''}^{B} F(\beta'\beta'')\sigma(\beta'')\{\beta''/\alpha'\} \tag{3d}$$

where

$$\sigma(\beta') = \int_A \{\alpha'/\beta'\}\, d\alpha' \{\beta'/\alpha'\} \tag{3e}$$

whence

$$\int_{-a}^{+a} \{\beta'''/\alpha'\}\, d\alpha' F(\alpha')\{\alpha'/\beta'\} = \int_{-\alpha}^{+a} \{\beta'''/\alpha'\}\, d\alpha' \sum_{\beta''}^{B} F(\beta'\beta'')\sigma(\beta'')\{\beta''/\alpha'\}\,. \tag{3f}$$

Now the $F(\beta'\beta'')$ defined by (3d) is always given by (3b). But if we write $\Delta\Theta(\beta') = \sigma(\beta')\{\alpha'/\beta'\}$ and make $a \to \infty$ we get from (3d), (3e) and (3f) just (3) and (3a) while (3b) remains true.

We may apply (3)–(3b) to find the transition probabilities induced in a system with continuous spectrum by an arbitrary perturbation. Let the system have initially the energy $E_0 = h\nu_0$ and the wave function $\{E_0/\alpha'\}$, and let the perturbation

$$V(\alpha' t) = \int_{-\infty}^{+\infty} V_\nu(\alpha') e^{2\pi i \nu t}\, d\nu \tag{4a}$$

set in at time T_0. The perturbed wave function after a time T is then, to a first approximation[5]

$$\{E_0/\alpha'\}e^{2\pi i\nu_0 t}-(2\pi i/h)\int_{-\infty}^{+\infty}d\nu\int_B^{\infty}d\beta'\int_{T_0}^{T}dtV_\nu(E_0\beta')\{\beta'/\alpha'\}e^{2\pi i(\nu-\nu)t}. \qquad (4\beta)$$

with $\nu=\nu(\beta')-\nu_0$.

From this we find, in the usual manner, for the probability that the system is in the range $\Delta\beta'$ at the time T

$$(4\pi^2/h^2)\int_A d\alpha'\left|\int_{-\infty}^{+\infty}d\nu\int_{\Delta\beta'}d\beta' V_\nu(E_0\beta')\{\beta'/\alpha'\}\int_{T_0}^{T}dt\,e^{2\pi i(\nu-\nu)t}\right|^2 \qquad (4)$$

By (3) this becomes

$$(4\pi^2/h^2)\int_{\Delta\beta'}d\beta'\left|\int_{-\infty}^{+\infty}d\nu V_\nu(E_0\beta')\int_{T_0}^{T}dt\,e^{2\pi i(\nu-\nu)t}\right|^2 \qquad (4a)$$

which is invariant under transformations of the form $\beta_1'=f(\beta')$, since, by(3b) the $[V_\nu(E_0\beta')]^2$ are contravariant to β'. If we now make $V_\nu=0$ except inside the range $\Delta\nu(\beta')$ and evaluate (4a) in the usual manner we find that outside $\Delta\beta'$ the number of systems does not grow, and that the total number within the range is for a large $T-T_0$

$$(4\pi^2/h^2)\,|\,V_\nu(E_0\beta')\,|^2\Delta\beta'\Delta\nu(\beta')(T-T_0). \qquad (4b)$$

This makes the rate at which systems enter the range

$$(4\pi^2/h^2)\,|\,V_\nu(E_0\beta')\,|^2\Delta\beta'\Delta\nu(\beta'). \qquad (4c)$$

Now we can, if we make $T-T_0$ very large, evaluate (4) by carrying out the integration with respect to ν first. Using Fourier's theorem we find instead of (4b)

$$4\pi^2/h^2\;|\,V_\nu(E_0\beta')\,|^2\Delta\beta' \qquad (4d)$$

for infinite T and T_0. Thus, in the steady state when there are (4d) systems in the range $\Delta\beta'$, the number entering the range per unit time is (4c).

We may expect, therefore, that the normalization (3) corresponds to making the number of particles leaving the system to infinity per unit time equal to $\Delta\nu$ for the range. We shall proceed to show this.

Let us limit ourselves at first to a single degree of freedom and let us suppose that the range of α is not quite infinite, so that some function of β', say $J(\beta')/h$, takes only integral values. We can then write in place of (3)

$$\int_A\{\alpha'/\beta'\}d\alpha'\int_{\Delta\beta'}d\beta''\{\beta''/\alpha'\}=1 \qquad (5a)$$

[5] Cf. E. Schroedinger, Ann. der Physik **81**, 117 (1926) Eq. 16. $V(E_0\beta')$ is the matrix component of V corresponding to the transition between the states $E=E_0$ and $\beta=\beta'$.

where β' lies in $\Delta\beta'$ and where $\Delta\beta'$ is a β' cell. The integral may be regarded as an integral taken over the cell, or as one to which only the integral values of J/h contribute. We may write (5a)

$$\tilde{\omega}=(1/h)(\partial J/\partial\beta') \tag{5b}$$

where

$$\tilde{\omega}=(1/h)\int_A d\alpha'\int_{\Delta\beta'}\{\alpha'/\beta'\}\,dJ(\beta')\{\beta'/\alpha'\}$$

is the total probability of finding the system in a β' cell. Setting $\beta'=J/h$ makes the probability uniform in phase space, but the range of integration $\Delta\beta'$ in (5a) does not vanish in the limit, and the limiting process is thus ambiguous. When we have $\{\beta'/\alpha'\}\sim Ce^{2\pi i\beta'\alpha'}$, however, this form of (5b) gives us $C=1$; and in this case Weyl's normalization means that the mean density per β' is assymptotically unity.

Now if we have $\partial J/\partial\beta'\to\infty$, then (5a) goes into (3) when we make $A\to\infty$; so that if we can interpret (5b) we shall know what (3) means. A simple way of doing this we get by setting

$$\partial J/\partial\beta'=h(\partial E/\partial J)^{-1}$$

and using

$$\dot{\omega}=\dot{\omega}(J)=\dot{\omega}(\beta')=\partial E/\partial J$$

which is quantum-mechanically true if ω is canonically conjugate to J. Then,

$$\tilde{\omega}\dot{\omega}=1 \tag{5c}$$

for

$$\beta'=E/h \tag{5d}$$

Now $\tau\tilde{\omega}\dot{\omega}$ is the flux across a surface $\omega=$const. with β value equal to β'; and setting $\beta'=E/h$ in (3) makes $\tilde{\omega}\dot{\omega}=1$. But we may show that $\tau\dot{\omega}$ is equal to the flux to (or from) infinity introduced above and given in terms of the wave functions[6] by

$$\sum\nolimits_\infty(\beta')=\sum(\beta')=h/2\pi m\,\mathrm{I}\left[\{\alpha'/\beta'\}(\partial/\partial\alpha')\{\beta'/\alpha'\}\right]$$

For $\sum(\beta')$ is a constant: it follows from the fact that the transformation equation for $\{\alpha'/\beta'\}$ is self-adjoint that $\sum_{\alpha'}(\beta')-\sum_{\alpha''}(\beta')=0$. Further, if β' is an integral of motion, $\tilde{\omega}\dot{\omega}$ is a constant independent of ω. Hence if $\sum=\tilde{\omega}\dot{\omega}$ is true at one point it is generally true. But we can make the forces vanish at some point $\bar{\alpha}$ without altering the motion appreciably; and then we have $\tilde{\omega}=f(\bar{\alpha})$ so that the flux across the $\omega=\tilde{\omega}$ surface is equal to that across $\alpha=\bar{\alpha}$ surface.

[6] This quantity was first introduced by M. Born, Zeits. f. Physik. **40,** 167 (1926), E. Schroedinger Ann. d. Physik. **81,** 109 (1926) and W. Gordon, Zeits. f. Physik. **40,** 117 (1926).

Hence setting $\beta' = E/h$ makes $\sum_\infty = 1$ and the flux to infinity in a range $\Delta\beta'$ becomes, in this case

$$\sum_\infty \Delta\beta' = \Delta E/h \tag{6}$$

Since $\sum_\infty \Delta\beta'$ does not depend upon the choice of β' this Eq. (6) holds generally, as was to be proved.

With problems of several degrees of freedom the coordinate α' maybe only half open ($a \leqq \alpha' \leqq \infty$ instead of $\infty \leqq \alpha' \leqq \infty$), and in this case $\{\beta'/\alpha'\}$ will be assymptotically given by two waves, one inward, and one outward, of equal amplitude. We then have $\sum_\infty = 0$ but $\sum_\infty^+ = \sum_\infty^- \neq 0$ to represent the two waves. One finds, in this case, that one must set $\sum_\infty^+ = \sum_\infty^- = 1$ for $\beta' = E/h$, so that in this case also both ingoing and outgoing waves have unit intensity per E/h. One can understand this most easily as follows: the transformation from α to ω is no longer one-valued so that, to any point in the (αJ) space there correspond two points in the (ωJ) phase space. The Weyl condition thus gives double the density in the (αJ) space that it would for an open coordinate. (This enters analytically in the integral (3) which goes only from a to ∞.)

One further point may perhaps be mentioned. In certain experiments, e.g., the photoelectric effect one may expect the flux inward from infinity to vanish, and only the flux outward to count: an atom emits electrons under the influence of light. In spite of this it is not justified to use for the aperiodic characteristic functions merely an outgoing wave. Analytically one sees this because the outgoing wave alone has a singularity at the origin. Physically it follows from the fact that in spectroscopic problems one specifies the energy of the hyperbolic orbit exactly; the phase is thus quite undetermined and one cannot say to which branch of the hyperbola (ingoing or outgoing) the electron will jump. In general each electron goes on both, since the orbit is closed at infinity.

When there are several continuous integrals β_1 one may set

$$\sum_\infty^{(i)} = 1 \tag{6a}$$

if one chooses

$$\Delta\beta_i' = (1/h)(\partial E/\partial\beta_i')_{\beta_j}\Delta\beta_i' \qquad i \neq j \tag{6b}$$

This gives a convenient rule, which is in practice easier to apply than (3), and which depends, as to be expected, only on the assymptotic behavior of the $\{\alpha'/\beta'\}$. In conclusion we may note that with (6b) the flux is given by

$$\int_A \Delta\Theta(\beta')\, d\alpha' \Delta\Theta^\dagger(\beta') \tag{Q}$$

and that the absorption coefficient for light is given by the square of the modulus of the matrix component of the perturbing energy.[7]

[7] One may regard the analysis of this section as a method of interpreting stationary solutions of the wave equation, in aperiodic problems, like collisions or photo-ionization. Cf. P. A. M. Dirac, Proc. Roy. Soc. **A114**, 256 (1927).

2. One may expect a motion of periodic systems to approach that given by the classical quantum theory when the action per cycle is large compared with h. Kramers[8] has shown that this condition makes the number of nodes between the limits of libration large, and has applied the approximation to show that half quantum numbers are better than integers. From Kramers' argument it appears that the essential condition for the validity of classical mechanics is that the number of nodes of the eigen-function should be large in a region in which the potential energy is sensibly constant. This condition, unlike that on the action per cycle, may be extended to aperiodic motions; in this paragraph we shall show that it enables one very simply to determine whether the classical formulae are valid for any problem that is susceptible of a quantum mechanical solution. The method will be applied to the scattering of an α-particle by a nucleus.

If one sets $e^{2\pi iS/h}$ in the wave equation one obtains

$$(h/2\pi i)\Delta^2 S+(\Delta S)^2+2M(E-\bar{U})=0 \tag{1}$$

The classical S satisfies

$$(\Delta S)^2+2M(E-\bar{U})=0 \tag{1a}$$

so that

$$\{E/x\}_{cl}=\exp(2\pi i(-2M)^{1/2}/h)\int ds(E-\bar{U})^{1/2} \tag{2}$$

These solutions (2) each correspond to a uniform distribution of particles when $E>\bar{U}$, and a rapid exponential drop at the edge of the geometrical shadow. Because of the interference of the $\{E/x\}$'s, however, this does not represent the distribution for any given experimental arrangement: e.g., one obtains the classical deflection pattern at an obstacle by combining the solutions (2) so as to give a plane incident wave.

Now when $|(h/2\pi)\Delta^2 S(\Delta S)^{-2}|$ is very small, S and therefore, $\{E/x\}$, will not have to be much modified to give the quantum mechanical solution; in this case, therefore, the classical formulae may be expected to retain an approximate validity. Qualitatively, we see that this condition can always be satisfied by taking S/h large enough, since $(\Delta S)^2$ is quadratic, $\Delta^2 S$ linear, in S/h. This is the old condition that quantum numbers shall be large, the wave-length small. We can make the condition more precise and bring out the optical analogy better, if we introduce

$$\lambda=(h/2\pi)\{2M(E-\bar{U})\}^{-1/2} \tag{3}$$

as the "wave-length" at a point. The condition that $\{E/x\}$ should be given approximately by (2) in a region then becomes

$$|\operatorname{grad}\lambda|<<1 \tag{4}$$

[8] H. A. Kramers, Zeits. f. Physik **39**, 828 (1926).

Now in any physical diffraction problem $\bar{U}$ will have singularities, and there will be points at which (4) will not be satisfied. There will thus be classical scattering if (and only if) these regions are immaterial for the diffraction pattern; that is, if one can set $\bar{U}=0$ within them without affecting a result appreciably.

As an example of this method we may consider the scattering of fast α-particles by nuclei. Here we have

$$\bar{U}=e_1e_2/r \tag{Q}$$

and

$$|\operatorname{grad}\lambda| = \left|\frac{\partial\lambda}{\partial r}\right| = \frac{e_1e_2}{2r^2}\left(E-\frac{e_1e_2}{r}\right)^{-3/2}\left(\frac{h^2}{8\pi^2M}\right)^{1/2} \tag{5}$$

If we make

$$r>>e_1e_2, \quad \text{say } r=Be_1e_2/E$$

we may replace (5) by

$$r^2E^{3/2}>>e_1e_2$$

and hence (4) can be satisfied outside of a sphere of radius

$$r_0=(c_1/E)(e_1e_2)^{1/2}[h^2E/8\pi^2M]^{1/4}$$

$$=c_2\lambda_\infty^{3/2}$$

where λ_∞ is the wave-length at infinity of the incident α-particle. Now the scattered wave, for large velocities, is given by

$$\{E/x\}_1=ce^{-ikr}\int_0^\infty \rho d\rho \int_0^\pi \sin\vartheta\, d\vartheta\, e^{2i\sin^2(\delta/2)\cdot\cos\vartheta\cdot\rho/\lambda}$$

$$=c\lambda^2e^{-ikr}\int_0^\infty \mu d\mu \int_0^\pi \sin\vartheta\, d\vartheta\, e^{2i\sin^2\delta/2\cdot\cos\vartheta\cdot\mu}$$

If we set $\bar{U}=0$ inside the sphere of radius r_0 we get

$$\{E/x\}_1'=c\lambda^2e^{-ikr}\int_{c_3\lambda_\infty^{1/2}}^\infty \mu d\mu \int_0^\pi \sin\vartheta\, d\vartheta\, e^{2i\sin^2(\delta/2)\cdot\cos\vartheta\cdot\mu}$$

so that, as $\lambda_\infty\to 0$

$$\{E/x\}_1'\to\{E/x\}_1$$

Hence the region in which (4) is not satisfied is, in the limit $v\to\infty$, immaterial so that Rutherford's formula must be expected to hold for this case.[9]

The argument may be extended to show that the quantum mechanical scattering approaches the classical scattering in the other limiting case,

[9] See P. M. S. Blackett, Proc. Camb. Phil. Soc. **23,** Part 6, 1927. J. R. Oppenheimer, Zeits. f. Physik **43,** 413 (1927).

where $v \to 0$. For the wave function drops off exponentially within a sphere of radius proportional to v^{-2}, whereas (4) is not satisfied within a sphere of radius proportional to $v^{-3/2}$. Setting $v=0$ within this latter sphere does not, therefore, in the limit $v \to 0$, affect the scattering. There is, however, no reason to suppose that for intermediate v the classical formulae hold.

3. If one separates the wave equation for a hydrogen atom in an homogeneous electric field in parabolic coordinates, one finds that one of the equations has a potential energy which becomes negatively infinite for infinite values of the coordinate. Such an equation has no quadratically integrable solutions, and no point spectrum.[10] There are thus no stable stationary states possible for a hydrogen atom in such a field.

If one encloses the atom in a large box, periodic motions, of course, become possible. If the field is now made very small, the solutions of the wave equation are very much like those for the unperturbed atom; but if the drop in potential across the box is comparable with the resonance potential of the atom this is no longer the case. We must, therefore, conclude that, under the customary experimental conditions the characteristic functions found by the perturbation method, which yield the Stark effect, are not the stationary solutions of the wave equation, and that they do not completely describe the effect of the field.

The physical interpretation of this result is very simple. If we imagine the potential energy U of the electron plotted along the direction of the field, we see that it falls from a very high value at one end of the box to a very low value at the other; this uniform fall is broken by a sharp drop due to the nucleus. On the low potential side of the nucleus there is a maximum, sharp inside but gradual outside. If, therefore, we specify the energy of this system, we cannot be certain that the electron is in the neighborhood of the nucleus; it may also be in the low potential part of the field. If we make the box infinite, then it becomes increasingly probable that we shall find the electron in this part of the field, and hence the motion becomes aperiodic. In the classical theory, however, this situation caused no difficulties; for we could specify the other coordinates of the electron (besides the energy), and thus make certain that it was near the nucleus; and it could not leave this region without getting enough energy to clear the maximum in U.

We have seen that this is not so in the quantum theory, and that there is no stationary state of interest. The electron will not stay indefinitely near the nucleus. This suggests the following question: Given the atom at time T_0 in, say, its normal state. The field is turned on. What is the probability that at a subsequent time T the electron will have left the atom for infinity? If $T-T_0$ is big enough, this probability will be indefinitely near to one; but we may presume that the rate at which it grows will be very small when the field is small. This presumption will be verified.

We could find the rate of ionization, of course, by computing exactly the characteristic function of the atom in the field as a function of the time and thus finding the rate at which the probability that the atom is outside

[10] H. Weyl, Math. Ann. **68,** 220 (1910).

a given sphere about the nucleus increases. There is, however, a simpler way of answering the question, which makes use of the fact that the two unperturbed characteristic functions, corresponding to the initial energy and representing, respectively, the atom in its unperturbed normal state, and the electron and nucleus flying apart under the influence of the field and with neglect of their attraction, are nearly orthogonal. It is therefore nearly, but not quite, unambiguous to ask whether the electron is bound or whether it is torn loose, since the chance that we might have to answer "both" is very small. This method of nearly orthogonal characteristic functions appears to be capable of fairly wide applications. We shall therefore first develop the general theory and then apply it to the ionization problem.

The system is initially in a given state of energy $E_0 = h\nu_0$, and the wave function[11] $\psi_0(x)$ satisfies

$$[H + H_0 - E_0]\psi_0(x) = 0 \tag{1}$$

At the time T_0 a perturbation $H_1(x)$ is introduced. Let

$$[H + H_1 - E_1]\psi_1(\nu_1 x) = 0\ ; \qquad E_1 = h\nu_1 \tag{2}$$

In general $E_1 = h\nu_1$ may be taken continuous; for unless (2) has characteristic values very close to E_0, the effect will not occur.[11a]

We now require that

$$|\epsilon_0|^2/|\Sigma_\infty(\nu_0)| << 1, \text{ where } \epsilon_0 = \int d\tau\psi_0(x)\psi_1^*(\nu_0 x) \tag{3}$$

Of course $\epsilon_\nu = \int d\tau\psi_0(x)\psi_1^*(\nu x)$ cannot always be small, since

$$\int d\nu \left| \int d\tau\psi_0(x)\psi_1(\nu x) \right|^2 = \int |\psi_0|^2 d\tau = 1$$

It is important to note that the ψ_1's are closed with respect to all functions analytic in the configuration space.

We may accordingly set for the wave function

$$\psi = \int a(\nu t)\psi_1(\nu x)e^{2\pi i\nu t}d\nu \tag{4}$$

The initial values of the a's are

$$a(\nu 0) = \epsilon_\nu \tag{4a}$$

We can now write

$$a(\nu t) = \epsilon_\nu e^{2\pi i(\nu_0 - \nu)t} + c(\nu t)$$

[11] We now write $\{E_0/x\} = \psi_0(x)$, etc.

[11a] For the singular case that (1) and (2) have identical discrete characteristic values, see F. Hund, Zeit. p. Physik, **43,** 805, 1927. [Note added to proof]

So that

$$\psi=\psi_0 e^{2\pi i\nu_0 t}+\int c(\nu t)\psi_1(\nu x)e^{2\pi i\nu t}d\nu \tag{4b}$$

The wave equation is

$$[H+H_0+H_1+(h/2\pi i)(\partial/\partial t)]\psi=0 \tag{5}$$

Setting (4b) in (5) we get

$$(h/2\pi i)\int c(\nu t)\psi_1(\nu x)e^{2\pi i\nu t}d\nu+H_1\psi_0(x)e^{2\pi i\nu_0 t}+\int c(\nu t)H_0\psi_1(\nu x)e^{2\pi i\nu t}d\nu=0 \tag{6}$$

If we expand in terms of the ψ_1's and make all the coefficients of (6) vanish. we get

$$(ih/2\pi)c(\nu t)-H_1(0\nu)e^{2\pi i(\nu_0-\nu)t}-\int c(\nu' t)H_0(\nu'\nu)e^{2\pi i(\nu'-\nu)t}d\nu'=0 \tag{6a}$$

Now in the first order we have by (4a) $c(\nu t)=0$ and therefore

$$c(\nu(t=(-2\pi i/h)\int_0^T H_1(0\nu)e^{2\pi i(\nu_0-\nu)t}dt \tag{6b}$$

Hence

$$|c(\nu t)|^2=(4\pi^2)h^2\,|\,H_1(0\nu)\,|^2\left|\int_0^T e^{2\pi i(\nu_0-\nu)t}\,dt\,\right|^2 \tag{6c}$$

for the number of systems in the state ν at the time T. Only when $\nu\sim\nu_0$ does this increase appreciably with T; the total increase in a little region about $\nu=\nu_0$ we get by integrating (6c) with respect to ν:

$$\Delta N(T)=(4\pi^2/h^2)\,|\,H_1(0\nu_0)\,|^2T \tag{7}$$

This is only significant, and therefore only accurate, to within a factor of the order of $\epsilon_0^2/\sum_\infty(\nu_0)$.

Because ϵ_0 is so small, $H_1(0\nu_0)$ may be much smaller than $H_1(0\nu)$ for some other ν. For this reason one cannot be certain that it is sufficient to take the first approximation in (6a), since, if one chooses T large enough to make the transitions sensibly conserve the energy, as in (7), $c(\nu t)$ may not be *very* small for some other ν.[12] From (6a) and (6b) follows, for the correction for the c_ν

$$c_\nu'=(-4\pi^2/h^2)\int d\nu'\int_0^T dte^{2\pi i(\nu'-\nu)t}\int_0^t dt'e^{2\pi i(\nu_0-\nu')t'}H_0(\nu'\nu)H_1(0\nu') \tag{8}$$

[12] This second order cascade is important in the theory of dispersion: see P. A. M. Dirac, Roy. Soc. Proc., **A114,** 710 (1927).

We may obtain a rough estimate of this, and thus of the error in (7), by the following method:

The only term in (8) that can grow large is

$$-\frac{1}{h^2}\int d\nu' \frac{H_0(\nu'\nu)H_1(0\nu')}{\nu'-\nu_0}\frac{1-e^{2\pi i(\nu_0-\nu)T}}{\nu-\nu_0} \tag{8a}$$

which has a vanishing denominator for $\nu=\nu_0$. Now $H_1(0\nu')$ is small for $\nu'\sim\nu_0$, since otherwise the second approximation is unnecessary, and it grows small again for very large ν', since the corresponding wave function has more and more nodes in the region in which ψ_0 differs appreciably from zero. There must therefore be some value $\bar{\nu}$ for which $H_0(\nu'\nu)\ H_1(\nu'\nu)$ has a maximum; only in the neighborhood of $\bar{\nu}$ will the integral contribute much to (8). If, now, the maximum is so sharp that the integrand of (8a) does not change sign within the essential part of the integral, we can estimate[13] the magnitude of the integral if we replace it, in (8a), by

$$[1/(\bar{\nu}-\nu_0)]\int d\nu' H_0(\nu'\nu)H_1(0\nu') \tag{8b}$$

For (8b) is easily evaluated by using

$$H_0(\nu'\nu)=\int d\tau\psi_1^*(\nu x)H_0(x)\psi_1(\nu' x) \tag{9a}$$

$$H_1(0\nu')=\int d\tau'\psi_1^*(\nu' x')H_1(x_1)\psi_0(x') \tag{9b}$$

If we now integrate directly with respect to ν and use

$$\int d\nu'\psi_1(\nu' x)\psi_1^*(\nu' x')=\delta(x-x') \tag{9c}$$

we get for (8b)

$$[-1/(\nu_0-\bar{\nu})]\overline{H_0H_1}(0\nu_0) \tag{10}$$

so that the second order effect may be roughly allowed for by writing

$$H_1(0\nu_0)+[1/h(\nu_0-\bar{\nu})]\overline{H_0H_1}(0\nu_0) \tag{10a}$$

for $H_1(0\nu_0)$ in (7). Now because ϵ_0 is small, H_0 will generally be small where H_1 is large, and conversely, so that the correction (10a) will not be very important. It is for this reason that the approximation introduced is permissible; if (10a) differed appreciably from $H_1(0\nu_0)$ it would be necessary to use the accurate expression (8) to find $\Delta N(T)$.

For the problem of the hydrogen atom in the field we take

$$H_0=-e^2/r\ ;\quad H_1=-eFz \tag{11}$$

[13] The method may give a good approximation even when this condition is not fulfilled.

with the field F along z. The normalized solution of (1) for the normal state is

$$\psi_0=[1/(\pi a^3)^{1/2}]e^{-r/a}=[1/(\pi a^3)^{1/2}]e^{-1/a(z^2+\rho^2)^{1/2}} \tag{12}$$

in the cylindrical polars z, ρ, ϕ. The wave equation for $\psi_1(\nu x)$ becomes

$$\Delta\psi_1+(\lambda+az)\psi_1=0 \tag{12a}$$

with

$$\lambda=8\pi^2\mu\nu/h=8\pi^2\mu E/h^2\ ;\qquad \alpha=8\pi^2\mu eF/h^2$$

and can be separated in z, ρ, ϕ.
The solutions take the form

$$u(\lambda_1\lambda_2\lambda_3)=e^{i\lambda_3{}^{1/2}\phi}J_{\lambda_3}{}^{1/2}(\rho_{\lambda_2}{}^{1/2})K(\gamma) \tag{12c}$$

here $\sqrt{\lambda_3}$ is integral, but λ_2 and λ_1 continuous and

$$\lambda=\lambda_1+\lambda_2+\lambda_3 \tag{12d}$$

Further $J_{\lambda 3}{}^{1/2}$ is Bessel's function of parameter $\lambda_3{}^{1/2}$, and

$$\gamma=(2/3\alpha)(-\lambda_1-\alpha z)^{3/2} \tag{12e}$$

Finally

$$K(\gamma)=\gamma^{1/3}H_{1/3}^{(2)}(-i\gamma) \tag{12f}$$

where $H_{1/3}{}^{(2)}$ is a solution of Bessle's equation with parameter $1/3$, and for $\gamma>0$ is the customary Hankel's function of the second kind; because of the double-valuedness of γ this becomes for imaginary γ

$$-i\gamma^{1/3}N_{1/3}\{(2/3\alpha)(\lambda_1+\alpha z)^{3/2}\} \tag{12g}$$

where $N_{1/3}$ is Neumann's cylinder function. We can thus describe the function K as follows: for $\gamma\gg 0$ it falls off exponentially

$$K(\gamma)\sim(2/\pi)^{1/2}\gamma^{-1/6}e^{5\pi i/12-\gamma} \tag{12h}$$

For $\gamma=0$ it has the value $i_2 2^{4/3}$. Its first zero occurs at $i\gamma\sim 2$. Beyond this it oscillates with decreasing amplitude and period, and for $\lambda_1+\alpha z\gg 0$ it is given by

$$(1/2\pi)^{1/2}\gamma^{-1/6}e^{i[(5\pi/12)+\gamma]}-e^{-i[(5\pi/12)+\gamma]} \tag{12i}$$

It differs from zero chiefly in the region $|\gamma|\leqq 2$.

The normalizing factors ξ for u are readily found. Since $\sqrt{\lambda_3}$ is integral, ξ_ϕ becomes $(2\pi)^{-1/2}$. Eq. 6 of Section 1 gives

$$\xi_\rho=2\pi(\mu/h)^{1/2}\ ;\qquad \xi_z=2^{4/3}\pi(\mu/h)^{1/2}(3\alpha)^{-1/6}$$

where $J_{\lambda_3}{}^{1/2}$ is normalized to $\Delta\nu_2=\dfrac{1}{\mathrm{b}}\dfrac{\partial \mathrm{E}}{\partial\lambda_2}\Delta\lambda_2$ and K to $\Delta\nu_1=\dfrac{1}{\mathrm{b}}\dfrac{\partial \mathrm{E}}{\partial\lambda_1}\Delta\lambda_1$, as in (6b). The normalizing factor thus becomes

$$\xi=(\mu/h)2^{11/6}\pi^{3/2}(3\alpha)^{-1/6} \tag{12j}$$

We can see now under what conditions the analysis of this section is applicable to the problem. The wave function which corresponds in energy to ψ_0 has

$$\lambda = -\lambda_0 = -\mu^2(2\pi e/h)^4$$

Since

$$\lambda_2 \geqq 0\ , \quad \lambda_3 \geqq 0, \quad \lambda_1 < -\lambda_0$$

Hence the argument γ of K vanishes at a point $z_0 \geqq \lambda_0/\alpha$; for $z < z_0$, γ is real. Hence if we choose the field small enough, $\psi_1(\nu_0 x)$ will be, in the neighborhood of the atom, as small as we want; conversely ψ_0 will be very small where $\psi_1(\nu_0\chi)$ is large. ϵ_0 can therefore be made very small, so that eq. (7) can be interpreted without ambiguity. Furthermore we can use (10a) to estimate the second order of cascade. For the essential part of the integral (8a) comes from values of λ for which the zero of γ lies close to the nucleus. For small field this corresponds to a very short ν range, and in this range the integrand does not in general change sign.

The matrix components of H_1 and H_0H_1 vanish when $\Delta\lambda_3 \neq 0$. We are interested in them only for $\lambda = -\lambda_0$, so that $\lambda_1 = -\lambda_0 - \lambda_2$, and the matrix components are functions of λ_2 alone. We can thus find, in accordance with (7) and (10a), $\Delta N(T,\lambda_2)$ and we can get the total ionization by integration;

$$\Delta N(T) = \int_0^\infty d\nu_2 \Delta N(T,\lambda_2) \tag{13}$$

The necessary matrix components thus become

$$H_1(\lambda_2) = -2eF\xi(\mu_1/a)(\pi/a)^{1/2} \tag{14}$$

$$\overline{H_0H_1}(\lambda_2) = 2e^3F\xi(\mu_2/a)(\pi/a)^{1/2}$$

with

$$\mu_1 = \int_0^\infty \rho d\rho J_0(\rho\lambda_2^{1/2}) \int_{-\infty}^\infty z dz e^{-(1/a)(z^2+\rho^2)^{1/2}} K(\gamma) \tag{14a}$$

$$\mu_2 = \int_0^\infty \rho d\rho J_0(\rho\lambda_2^{1/2}) \int_{-\infty}^\infty z dz e^{-(1/a)(z^2+\rho^2)} K(\gamma)/(z^2+\rho^2)^{1/2}$$

We may estimate these integrals as follows:
We have in the first place

$$\mu_1 = -[\partial/\partial(1/a)]\mu_2 \tag{15}$$

so that it is enough to find the μ_2. Now we can see at once that μ_2 will be largest for small values of λ_2, and that, for small α, it falls off rapidly as λ_2 increases; for the value of $e^{-1/a(z^2+\rho^2)^{1/2}}$ at $\gamma = 0$ becomes much smaller, as does that of $K(\gamma)$ at $z = 0$, as λ_2 grows. But

$$\mu_2 = a\int_{-\infty}^\infty z dz e^{-|z|/a} \cdot K(\gamma) + a\lambda_2^{1/2} \int_{-\infty}^\infty z dz \int_0^\infty d\rho e^{-(1/a)(z^2+\rho^2)^{1/2}} \cdot J_1(\rho\lambda_2^{1/2}) \cdot K(\gamma) \tag{16}$$

and since $J_1(0)=0$ we may neglect the second term. (The corresponding term in μ_1 is also negligible).

The integral with respect to z is easy to estimate. For, from the properties of K it follows that the main part of the integral is contributed by the stretch $z \leqq z_0 = \lambda_0 + \lambda_2/\alpha$:

$$\mu_2 \sim a \int_{-\infty}^{z_0} z dz e^{-|z|/a} \cdot K(\gamma) \tag{16a}$$

Before we evaluate this, we can show that μ_2 is negligible compared to μ_1.

$$\mu_1 = a \int z \,|\, z \,|\, dz e^{-|z|/a} \cdot K(\gamma) + a^2 \int z dz e^{-|z|/a} \cdot K(\gamma) \tag{16b}$$

The term with $|z|$ is obviously large for small α. In this case therefore the cascade effect proves unimportant compared to the direct transition. For small α and λ_2 the second term in (16b) yields

$$\mu_1 \sim a\Gamma e^{-(2/3\alpha)(\lambda_0+\lambda_0)^{3/2}} \cdot (\lambda_0+\lambda_2)^{9/16} \alpha^{-11/8} \tag{17}$$

$$\Gamma = 2^{9/4} e^{-3/4} \Gamma(3/4)/\Gamma(1/2)\Gamma(15/4)$$

In (13) this gives, with (14a) and (12j) and neglecting higher powers of α

$$\Delta N(T) = (\Gamma/24)(h/m) a^{-5/4} \alpha^{1/4} e^{-(4/3)a^{-3}\alpha^{-1}} \cdot T \tag{18}$$

which is the required result.

The rate at which a field of 1 volt per cm dissociates a hydrogen atom is thus $1/10^{10^{10}}$ per sec. The true resistance of 1 cm^3 of gas at 0,001 mm in this field is about $10^{10^{10}}$ ohms. The values of the field for which the dissociation becomes appreciable are of the order of

$$F \sim 5 \times 10^7 \text{ e. s. u.}$$

which is about a tenth of the field which makes the classical Bohr orbit unstable.

The effect increases very rapidly with a drop in the ionization potential of the atom, so that we should expect it to be particularly marked for certain metallic atoms at the surface of a conductor. The aeona effect, or pulling of electrons out of metal by fields of the order of 10 ^{5}e. s. u., is probably to be accounted for in this way.[13a]

The importance of effects of the kind here considered is, however, that they restore to the atom some of the classical instability which was destroyed by the quantum conditions. For instance we can now understand a little better the mechanism of metallic conduction. The ionization potential of metallic atoms is characteristically low, so that the valence electrons will be

[13a] This is confirmed by the fact, that when one uses the data of R. A. Millikan and C. Eyring, This Journal, **27**, p. 55, Fig. 2, 1926, to plot the reciprocal of the field against the logarithm of the current minus one fourth the logarithm of the field, the points so obtained lie on a straight line. For this result follows from (18).

pulled out easily by the fields of neighboring atoms, (and, to a less extent, by external fields). If the probability of ionization is large, we shall no longer be justified in associating an electron with a single ion, and in this sense the valence electrons will be free. We have seen that this probability is greatly decreased if the threshold that the electron must clear is raised. If, therefore, the atoms of the metal are separated, e.g. by heat or by distortion, the passage of the electrons through the metal will be greatly hindered. It is known[14] that one can give a fairly satisfactory account of metallic conduction, if one assumes that it is the "gaps" in the atomic lattice which account for the resistance of the metal.

The transitions involved in a chemical reaction are of the kind considered in this section. In particular, one can easily write down the probability that an electron will be captured from a hydrogen atom by a passing α-particle; but the integrals which occur are awkward to evaluate.

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[14] P. W. Bridgmar Rap. du Con. Solvay, Bruxelles, 1924.